Int J Ind Chem (2014) 5:6
DOI 10.1007/s40090-014-0006-8

RESEARCH

Modification of copolymers using nucleophilic reactions between glycidyl methacrylate and 9-anthracene carboxylic acid

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Received: 15 January 2013 / Accepted: 19 December 2013 / Published online: 8 March 2014

Abstract Epoxide ring opening reaction is a route that explains the chemical modification of glycidyl methacrylate (GMA) polymers with nucleophilic reagent containing hydroxyl, carboxyl or amine groups. In this work copolymers of GMA have been modified by incorporation of bulky 9-anthracene carboxylic acid groups. The glycidyl methacrylate polymers were prepared by radical copolymerization of GMA methyl, methacrylate, ethyl methacrylate, methyl acrylate and butyl acrylate mixtures. The polymers were modified through epoxy functional groups in two steps: (i) the glycidyl methacrylate copolymers were dissolved in *N,N*-di-methyl formamide; (ii) 9-anthracene carboxylate salt was added to the copolymers solutions prepared in step (i). The structure of all the resulting polymers was characterized and confirmed by FT-IR and ^{1}H-NMR spectroscopic techniques. The presence of bulky 9-anthracene carboxylate groups in polymer side chain leads to different applications in the polymer industry and also a series of novel modified polymers are obtained.

Keywords Glycidyl methacrylate · 9-Anthracene carboxylic acid · Ring opening · Modified polymer

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Introduction

Glycidyl methacrylate (GMA) has a high tendency for homopolymerization and copolymerization with other monomers [1–3]. The copolymers of glycidyl methacrylate can be prepared by a variety of methods. Generally, a free radical initiator is needed to induce a polymerization reaction. It is confirmed that GMA undergoes radical polymerization exclusively on its methacrylic double bond, with the oxirane function remaining unaffected [4–6]. The interest in glycidyl methacrylate copolymers has been continuously growing, due to their successful application in various industrial processes [7]. Copolymers of glycidyl methacrylate are commercially available, bearing reactive epoxide groups; these epoxide groups present in the polymer chain can easily undergo an opening reaction with nucleophilic reagents which contain hydroxyl, carboxyl, trisyl or amine groups [8–15]. The Diels–Alder reaction between anthracene and maleic anhydride to form 9,10-dihydroanthracene-9,10-α,β-succinic anhydride was successful and occurred via the Diels–Alder mechanism. Anthracene served as the dien and maleic anhydride was the dienophile [16–18]. There already exist examples of some interesting polymers that are modified by 9-anthracene carboxylic acid group [19]. These anthracene groups could take part in cycloaddition reaction with other functional groups such as anhydrides and quinones. The compositions can be applied to dielectric layers, so as to minimize or prevent reflection during the dual damascene process while simultaneously blocking via photoresist poisoning, which commonly occurs when organic anti-reflective coatings are applied to low dielectric constant layers [20, 21]. The main aim of this paper is the development, synthesis and characterization of modified glycidyl methacrylate polymers with 9-ACA. Also, the thermal properties of the obtained polymers have been studied.

Table 1 The condition of preparation of copolymers I–IV

Sample	Monomer 1	Monomer 2	Amount of monomer 1 (mmol)	Amount of monomer 2 (mmol)	Time (h)
I	GMA	MMA	20	20	24
II	GMA	EMA	20	20	24
III	GMA	MA	20	20	24
IV	GMA	BA	20	20	24

Experimental

Instrument

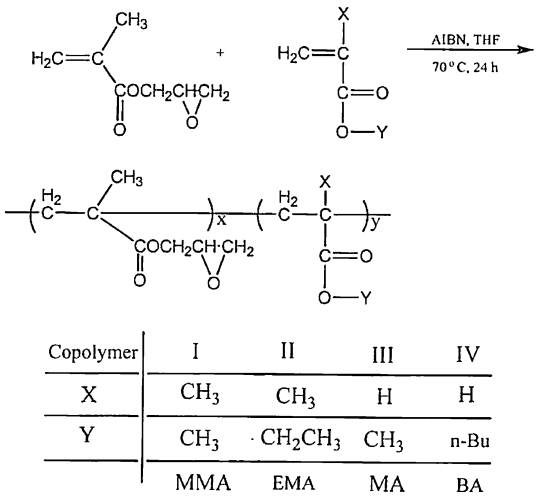
The infrared spectra were recorded on Bruker spectrometer scientific 400 IR. ^{1}H-NMR spectra were run on a Bruker 250 MHz spectrometer at room temperature using $CDCl_3$ and DMSO-d6 as solvents and TMS as internal standard. Dynamic mechanical thermal analysis (DMTA) was characterized by Triton (Tritec 2000 DMN) with the rate of 10 °C/min.

Materials

9-Anthracene carboxylic acid was obtained from Merck Chemical Company. The radical initiator of azobis (isobutyronitrile) (AIBN) was purchased from Fluka and purified by recrystallization from absolute ethanol. Methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), butyl acrylate (BA) and glycidyl methacrylate (GMA) were obtained from Merck and distilled under reduced pressure to remove inhibitors before use. Benzyltriethyl ammonium chloride (BTAC) was obtained from Merck Chemical Company. *N,N*-di-methyl formamide (DMF. Merck) and tetrahydrofuran (THF) were dried over anhydrous $MgSO_4$ for 2 days and distilled under reduced pressure.

Synthesis of the acrylic copolymers and methacrylic copolymers (I–IV)

Poly(GMA-co-MMA) (I), poly(GMA-co-EMA) (II), poly(GMA-co-MA) (III) and poly(GMA-co-BA) (IV) were synthesized by a general method using 2 g (20 mmol) of methyl methacrylate, 2 g (20 mmol) of ethyl methacrylate, 1.73 g (20 mmol) of methyl acrylate or 2.56 g (20 mmol) of butyl acrylate and also a mixture of 2 g (20 mmol) of GMA and 0.065 g (0.4 mmol) of AIBN in 15 mL of tetrahydrofuran (THF). The reaction mixture was heated to 70 ± 1 °C with constant stirring under a nitrogen atmosphere. The reaction conditions were maintaind for 24 h.



Copolymer	I	II	III	IV
X	CH_3	CH_3	H	H
Y	CH_3	CH_2CH_3	CH_3	n-Bu
	MMA	EMA	MA	BA

Scheme 1 Synthesis of copolymers I–IV

Polymer solutions were poured dropwise into a large excess of methanol. The obtained polymer was purified by precipitating twice into methanol. The polymer was filtered and dried under vacuum at room temperature. The reaction condition is shown in Table 1 and Scheme 1.

^{1}H-NMR and FT-IR spectra of polymers I–IV

I FT-IR (KBr) ν cm^{-1}: 3,001.61, 2,953(C–H aliphatic), 1,731.67(C=O), 1,267.74, 1,148.

(C–O stretch in ester), 907.31(C–O epoxide ring).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.75-0.93(s,6H), 1.42–1.72(s,4H), 2.64(br,1H), 2.76(br,1H), 3.24 (br,1H), 4.05(br, 1H), 4.25(br,1H), 3.31(s, 3H).

II FT-IR (KBr) ν cm^{-1}: 2,995.92, 2,949.17(C–H aliphatic), 1,730.57(C=O), 1,262.38, 1,150.96 (C–O stretch in ester), 908.17(C–O epoxide ring).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.93–1.1(m,9H), 1. 16–1.75(s,4H), 2.63(br,1H), 2.78(br,1H), 3.21 (br,1H), 3.65(br, 1H), 3.93(br, 1H), 4.34(s,2H).

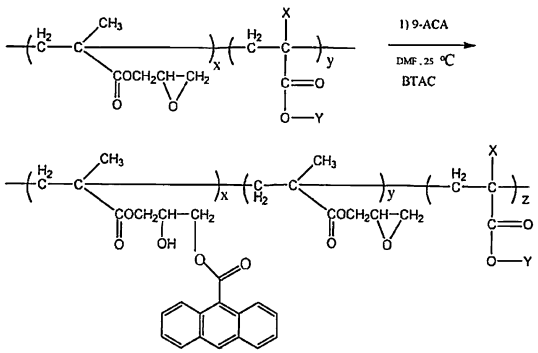
III FT-IR (KBr) ν cm^{-1}: 1,734.43(C=O),

1,264.47,1,125.43(C–O ester), 907.14(C–O epoxide) 2,924.72, 2,854.38 (C–H aliphatic).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.35–1.4(s, 3H), 1.47–1.81(s, 5H), 2.6(br,1H), 2.8(br,1H), 3.1(br,1H), 3.6(br,1H), 4.2(br, 1H), 3.3 (s, 3H).

IV FT-IR (KBr) ν cm^{-1}: 2,956.43, 2,877.48(C–H aliphatic), 1,731.05(C=O), 1,258.26, 1,164.66 (C–O stretch in ester), 908.61(C–O epoxide ring).

^{1}H-NMR ($CDCl_3$, TMS, 250 MHz) δ ppm: 0.8–1 (s, 6H), 1.3–1.5(br, 5H), 1.8–2.1(4H), 2.69 (br,1H), 2.76(br,1H), 3. 1(br, 1H), 3.7(br,2H), 3.9 (br, 1H),4.29 (br, 2H).



Copolymer	I	II	III	IV
X	CH_3	CH_3	H	H
Y	CH_3	CH_2CH_3	CH_3	n-Bu
	MMA	EMA	MA	BA

Scheme 2 Reaction of copolymers I–IV with 9-ACA

Attachment of 9-anthracene carboxylate group to the side chain of copolymers

Benzyltriethyl ammonium chloride (BTAC) (5.2 mmol, 1.2 g) was slowly added to 9-anthracene carboxylic acid (5.2 mmol, 1.2 g) dissolved in 15 mL of DMF at room temperature while stirring the mixture under a nitrogen atmosphere for 30 min. Then, 3.5 mmol of epoxide-containing monomer unit of polymers ^{I}ACA–^{IV}ACA (0.5, 0.5, 0.5, 0.5, g) of polymers, respectively, in 15 mL of DMF was added dropwise within 1 h. The contents were kept at ambient temperature for another 24 h while stirring. The mixture was then poured dropwise into a large excess of cold acidic water (5 %). The precipitated solid was recovered by filtration, washed successively with diethyl ether and then dried in vacuum at room temperature for 48 h (Scheme 2).

The molar percentage of modified copolymers is given in Table 3.

^{1}H NMR and FTIR spectra of polymers ^{I}ACA–^{IV}ACA

^{I}ACA FTIR (KBr) ν cm^{-1}: 3,439.25(stretch of O–H), 1,679.64(C=O ester), 1,727.87 (C=O aromatic), 1,520 (C=C stretching of aromatic ring), 1,253–1,174.4(C–O ester).

^{1}H-NMR (DMSO-d6, TMS, 250 MHz) δ ppm: 0.75–0.93(s,9H), 1.2–1.72(br,6H), 2.64 (br,1H), 2.76 (br,1H), 3.24(s,1H), 3–4.4 (br, 8H), 5.5 (OH), 7.5–8.6(m,9H).

^{II}ACA FTIR (KBr) ν cm^{-1}: 3,447.57 (stretch of O–H), 1,678 (C=O ester), 1,727.52 (C=O aromatic), 1,590 (C=C stretching of aromatic ring), 1,254.81–1,149.24(C–O ester).

^{1}H-NMR (DMSO-d6, TMS, 250 MHz) δ ppm: 0.93–1.1(m,12H), 1.16–1.75(br,6H), 2.63(br,1H), 2.78(br,1H), 3 (s,1H), 3–4.4(br, 7H), 5.5(OH), 7.4–8.9(m,9H).

^{III}ACA FTIR (KBr) ν cm^{-1}: 3,449.11 (stretch of O–H), 1,678.47(C=O ester), 1,732.68 (C=O aromatic), 1,557–1,521(C=C stretching of aromatic ring), 1,256–1,170(C–O ester).

^{1}H-NMR (DMSO-d6, TMS, 250 MHz) δ ppm: 0.2–1.4(br, 6H), 1.47–1.81(br, 7H), 2.6(br,1H), 2.8(br,1H), 3.1(br, 1H), 3–4.4(br,8H), 5.5(O–H), 7.2–8.9 (m,9H).

^{IV}ACA FTIR (KBr) ν cm^{-1}: 3,421.52 (stretch of O–H), 1,676.79 (C=O ester), 1,730.86(C=O aromatic), 1,521.11 (C=C stretching of aromatic ring), 1,255.81–1,148.33(C–O ester).

^{1}H-NMR (DMSO-d6, TMS, 250 MHz) δ ppm: 0.8–1 (m, 9H), 1.3–1.5(7H), 1.8–2.1(4H), 2.69 (br,1H), 2.76 (br,1H), 3. 1(br, 1H), 3–4.4(br,7H), 5.5(OH), 7.4–8.9(m, 9H).

Results and discussion

The presence of oxirane group in GMA polymers and copolymers favors further chemical modification for various applications [7]. The monomer of GMA was copolymerized with methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA) and butyl acrylate (BA) by free radical copolymerization in THF solution. The chemical structure of the related polymers is represented in Figs. 1 and 2. The resulting polymers are soluble in polar aprotic solvents (e.g., DMF, DMSO, THF) and chlorinated solvents (e.g., chloroform and methylene chloride), but insoluble in solvents containing hydroxyl groups such as methanol, ethanol and 2-propanol. In this work copolymers of GMA have been modified by incorporation of bulky 9-ACA groups. The resulting modified polymers are soluble in polar aprotic solvent DMF and DMSO, but insoluble in solvent chloroform and methylene chloride. The presence of the epoxy group in GMA leads to modification of copolymers for various applications. In recent years, studies have been carried out about the attachment of 9-anthracene carboxylic acid to polymers. Also, there is some information about the effects of these groups on the polymers' properties. Several types of 9-ACA reaction with different compounds have been given. One of these reactions is the epoxide ring reaction with 9-ACA, in which the produced compound has many applications in the preparation of dielectric thin layers. Another reaction of 9-ACA with polymers containing 4-chloromethyl styrene has been investigated [19–21]. We have succeeded in preparing polymers having side chains containing 9-anthracene carboxylate groups that strongly

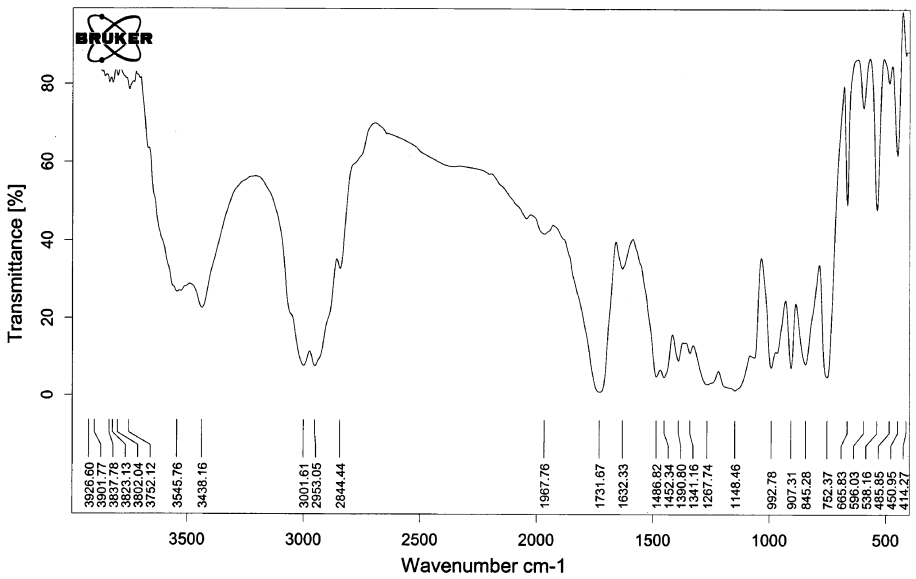


Fig. 1 Infrared spectra of poly(GMA-co-MMA)

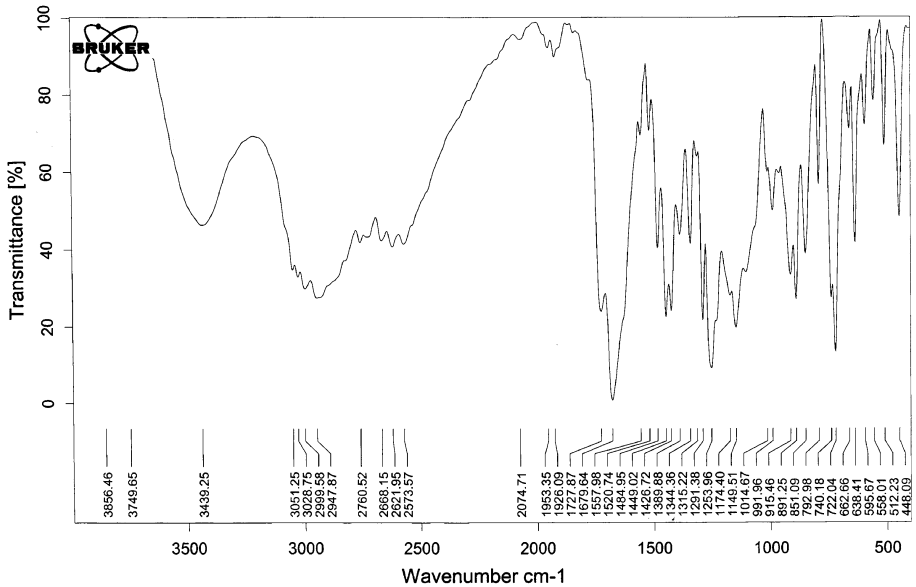


Fig. 2 Infrared spectra of poly(GMA-co-MMA) after reaction with 9-ACA

affect the properties of the polymers. The assignment of the resonance peaks in the ^{1}H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. The proton resonances of the –COOCH2–group in copolymers GMA with EMA and BA at 3.7–4.3 ppm and the proton resonances of the –COOCH3 group in copolymers GMA with MMA and MA at 3.3 ppm and those of the epoxide group in GMA at 3.27, 2.88 and 2.7 ppm have been clearly resolved. The copolymers' compositions were calculated from the H-NMR spectra data. In the past few decades, $_{1}$H-NMR spectroscopic analysis has been established as a power tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity [22]. The molar compositions of GMA and MMA, EMA, MA and BA in copolymers were calculated from the integrated ratio. Let m_1 be the mole fraction of GMA and m_2 that of the other monomer. GMA contains three epoxide protons; EMA and BA contain two methylene protons; and MMA and MA contain three methyl protons. The following expression is used to determine the composition of copolymers I and III (Table 2):

Table 2 Molar percentage of copolymer making monomers

Copolymer	*m*1 (%)	*m*2 (%)
Poly(GMA-co-MMA)	50	50
Poly(GMA-co-EMA)	46	54
Poly(GMA-co-MA)	55	45
Poly(GMA-co-BA)	58	42

$$\frac{\text{Integrared peak area of } 2.7-3.27 \text{ ppm}}{\text{Integrared peak area of } 3.3 \text{ ppm}} = \frac{3m_1}{3m_2} = A$$

$$m_1 + m_2 = 1$$

and the following expression is used to determine the composition of copolymers II and IV (Table 2):

$$\frac{\text{Integrared peak area of } 2.7-3.27 \text{ ppm}}{\text{Integrared peak area of } 3.7-4.3 \text{ ppm}} = \frac{3m_1}{2m_1 + 2m_2} = A$$

$$m_1 = \frac{2A}{3}$$

Characterization of copolymers I–IV before and after modification with 9-ACA

Infrared spectra

The asymmetrical and symmetrical stretching due to the methyl and methylene groups in copolymers I–IV are observed at 2,953 and 3,001 cm^{-1}. The band at 1,731 cm^{-1} is attributed to the ester carbonyl stretching of GMA and comonomers MMA, EMA, MA and BA units. Another band seen at 907 cm^{-1} is due to the asymmetric stretching of the epoxy group. The bands of 1,148 and 1,267 cm^{-1} are attributed to the ester C–O stretching of GMA and comonomers MMA, EMA, MA and BA units; for example, IR spectra of copolymer (GMA-co-MMA) are shown in Fig. 1. The infrared spectra of the modified products show the broadbands characteristic of the hydroxyl groups at wave number 3,447 cm^{-1} which is indicative of the ring opening reaction. Aromatic = C–H bands appeared at 3,051 cm^{-1}. The bands at 1,679 and 1,730 cm^{-1} are attributed, respectively, to the ester carbonyl stretching of GMA, comonomers MMA, EMA, MA and BA and aromatic ring. The IR spectrum of poly(GMA-co-MMA) with 9-ACA has been shown in Fig. 2.

^{1}H NMR spectra

^{1}H NMR spectra of copolymers I–IV showed two signals at 4.25 and 3.6 ppm due to the splitting of methylene protons in the CH2O– group attached to the carbonyl group of the GMA group. The peak at 3.2 ppm is due to the methyne proton of the epoxy group. The methylene protons of the epoxy group show signals at 2.64 and 2.76 ppm. The resonance signal at 4.29 ppm was attributed to two methylene protons of –COOCH2 in copolymer BA. The resonance signal at 3.3–3.5 ppm was attributed to three methyl protons of –COOCH3 in copolymers MMA and MA. The broad signal at 0.75–1.4 ppm was due to

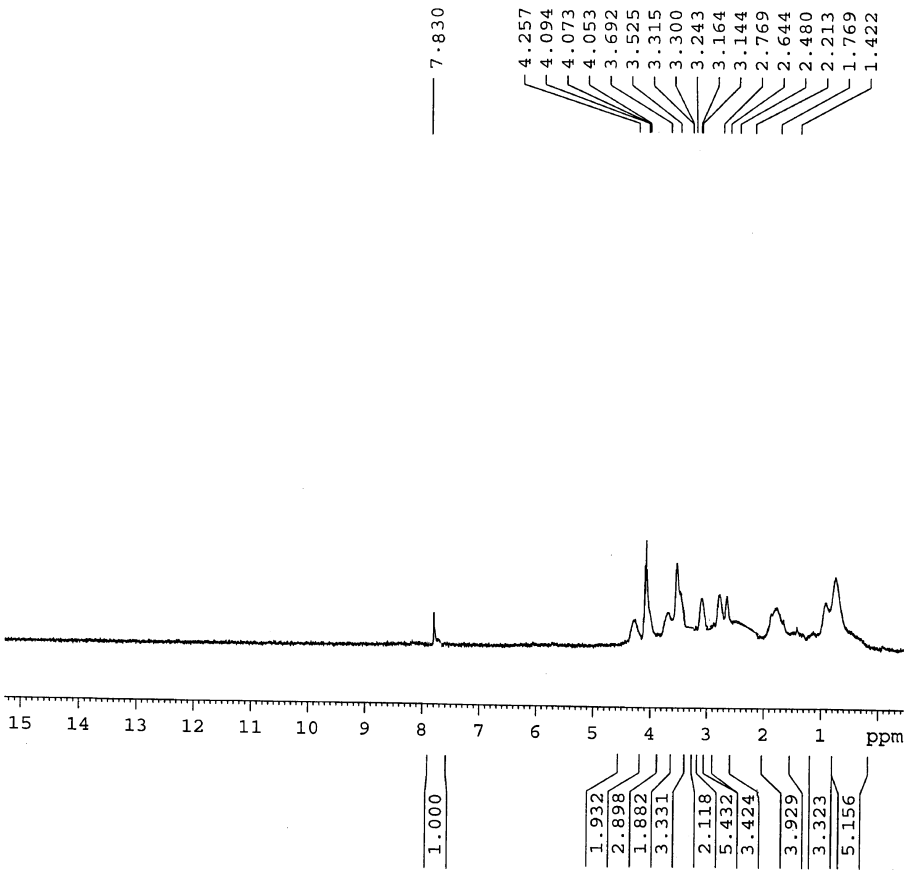


Fig. 3 ^{1}H NMR spectra of poly(GMA-co-MMA)

the methylene groups of backbones and other alkyl groups. For example, the ^{1}H-NMR spectra of copolymer (GMA-co-MMA) are shown in Fig. 3. The 1H NMR spectra of the pure and modified polymers show epoxy groups ($\delta = 2.64$–3.24 ppm), which are well defined in the unmodified polymers but decrease after modification. According to these results, part of the epoxy groups were modified and created random polymers. The peaks at 3–4.4 ppm is due to the methyne proton attached to the alcohol group, methylene protons in the –CH2O– group attached to the carbonyl group of the GMA and protons in the –CH2– group attached to the 9-anthracene carboxylate group of GMA. The peaks at 7–9 ppm are due to the 9-ACA protons. The H-NMR spectrum of poly(GMA-co-MMA) with 9-ACA has been shown in Fig. 4.

DMTA curve

Glass transition temperature is one of the most essential properties of polymers, dictating important features such as thermomechanical behavior and processing conditions. In the context of microphase separation, for example, reaching the thermodynamically stable, microphase-separated structure requires overcoming the glass transition temperature (Tg) (either by annealing or lowering the Tg by solvent vapor) to allow chain mobility. The Tg of polymers was determined by dynamic mechanical thermal analysis [22] (Table 3). All the synthesized polymers show a single Tg. DMTA scans show that the presence of bulky 9-anthracene carboxylic acid groups lead to a decrease in the glass transition temperature from 132 to 90 °C for polymer I and from 93 to 67 °C for polymer II, and an increase in the Tg from 36 to 45 °C for copolymer III and from 26 to 38 °C for copolymer IV. The study of the thermal properties of the obtained polymers by DMTA curves showed that Tg of the acrylate sample (including MA and BA) is increased after the reaction with 9-ACA. This may be attributed to the stiff aromatic rings as well as the possibility of hydrogen-bonding formation of OH groups created after the modification with 9-ACA (H-bonding of OH with the adjacent chain functional groups of O–H and C=O).Conversely, Tg of methacrylate samples (including MMA and EMA) is decreased after the reaction with 9-ACA. It can be partially related to the steric hindrance of the methyl groups in samples $I_{9\text{-ACA}}$ and $II_{9\text{-ACA}}$. The presence of CH_3 groups on the main chain disfavors

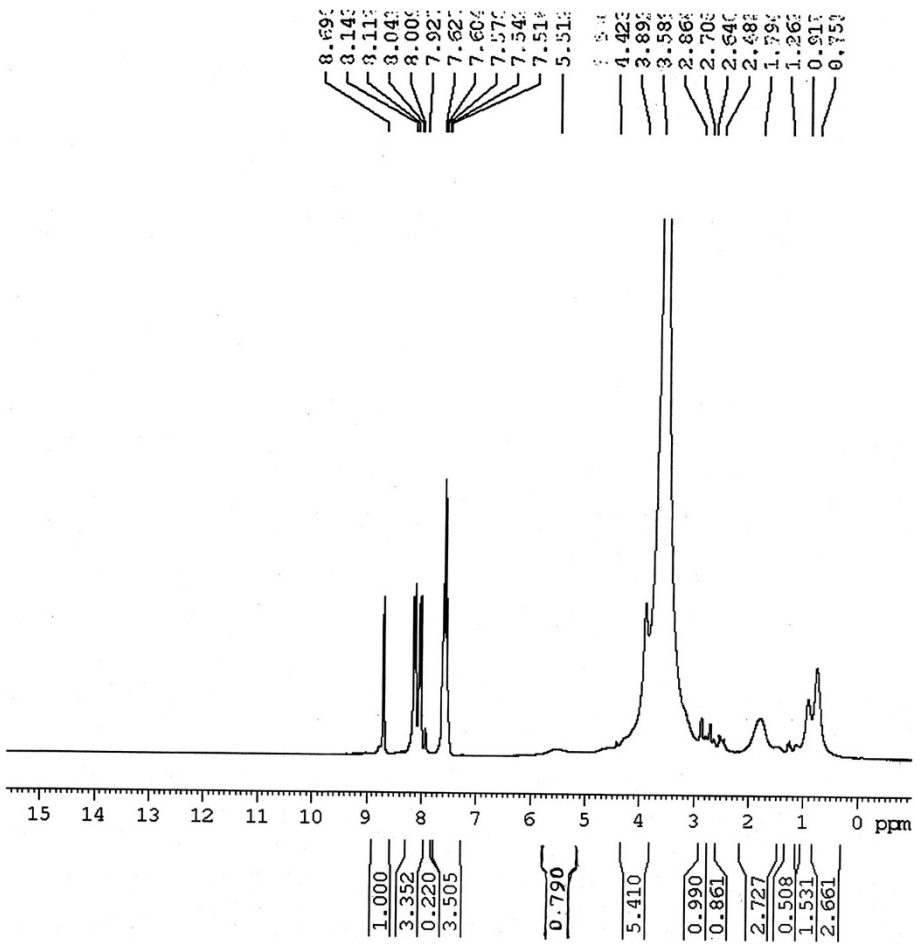


Fig. 4 ^{1}H NMR spectra of poly(GMA-co-MMA) after reaction with 9-ACA

Table 3 Glass transport temperature of polymers

Copolymer	*Tg* (°C): before modified	*Tg* (°C): after modified
Poly(GMA-co-MMA)	132	90
Poly(GMA-co-EMA)	93	67
Poly(GMA-co-MA)	36	45
Poly(GMA-co-BA)	26	38

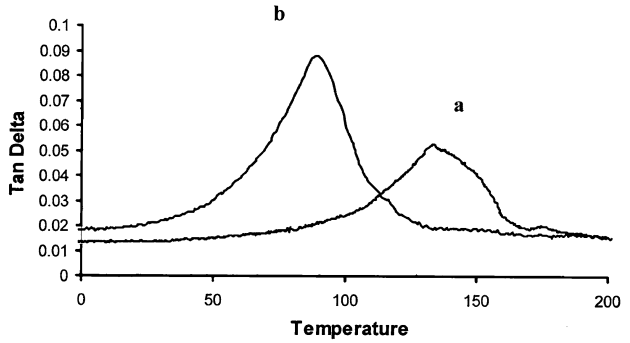


Fig. 5 DMTA curves of poly(GMA-co-MMA) **a** before reaction with 9-ACA and **b** after reaction with 9-ACA

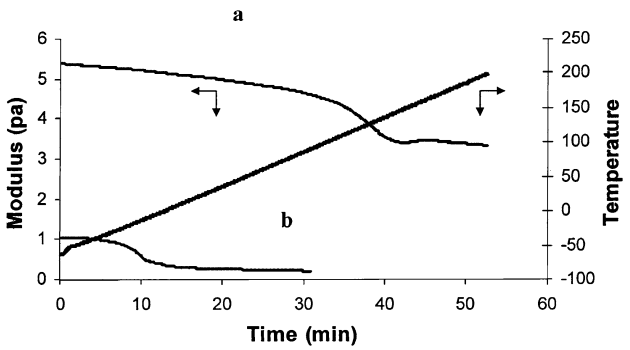


Fig. 6 Modulus curves of poly(GMA-co-MMA) **a** before reaction with 9-ACA and **b** after reaction with 9-ACA

the H-bonding formation. Epoxide and anthracene rings in polymers increase the *Tg* and rigidity. On the other hand, opening the epoxide ring increases the micro-Brownian movements and results in decreasing *Tg*. In methacrylate copolymers, opening the rings prevail on anthracene rings, but in acrylate copolymers it is just the opposite (Fig. 5).

Modulus curve

Modulus is one of the mechanical properties that demonstrate a material's resistance against deformation under load. The flexural modulus (FM), in particular, measures this behavior under simple beam loading. Variation of modulus with temperature for copolymers of GMA and modified copolymers with 9-anthracene carboxylic acid has been shown in Fig. 6. A considerable decrease in modulus was observed for modified poly(GMA-co-MMA) and poly(GMA-co-EMA) and increase in modulus observes for modified poly(GMA-co-MA) and poly(GMA-co-BA) with respect to modified copolymers of GMA. The time dependence of modulus for the copolymers of GMA and modified copolymers at the temperature interval −50 to 350 °C and with a constant slope (10 min/ °C) also shows a similar pattern. The dynamic properties of GMA copolymers and its modified copolymers with 9-anthracene carboxylic acid at various temperatures are summarized in Table 4.

Table 4 Modulus change in synthesized polymers

Copolymers	Modulus change			
	0 °C	20 °C	40 °C	60 °C
Poly(GMA-co-MMA)	5.31	5.01	4.92	4.81
Poly(GMA-co-MMA) with 9-ACA	1.03	1.02	0.99	0.91
Poly(GMA-co-EMA)	3.78	3.70	3.60	3.48
Poly(GMA-co-EMA) with 9-ACA	1.27	1.24	1.18	1.06
Poly(GMA-co-MA)	0/74	0.72	0.59	0.42
Poly(GMA-co-MA) with 9-ACA	1.01	0.93	0.72	0.55
Poly(GMA-co-BA)	0.49	0.39	0.27	0.25
Poly(GMA-co-BA) with 9-ACA	1.39	1.24	0.91	0.62

Conclusion

In recent years, polymers based on glycidyl methacrylate have received increasing attention owing to their versatile applications. The present paper reports the synthesis, spectroscopic and thermal characterization of glycidyl methacrylate polymers and copolymers containing very bulky 9-anthracene carboxylic acid as side chains.

The copolymers of GMA with different methacrylic and acrylic monomers were synthesized by free radical solution polymerization and the composition calculated by the corresponding H-NMR analysis. GMA copolymers containing epoxy side groups have been modified by 9-ACA via ring opening reaction. In these cases, parts of the epoxy groups react. Such a dramatic reactivity decrease is likely due to the close proximity of the epoxy groups, which leads to a close packing of moieties. Study of the DMTA curves of the polymers indicated that glass transition temperature values of all the copolymers I and II decreased and the copolymers III and IV increased with incorporation of

9-ACA groups as side chains. The presence of the 9-ACA groups into polymer structures increases the rigidity of macromolecules and creates modified polymers with novel properties.

Acknowledgments The authors thank the Islamic Azad University of Ardabil Branch for technical support during this research.

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